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Cyanide, cyanate, and thiocyanate, separately or in combination with other wastes, frequently are waste water problems. Several treatment methods are available for cyanide; some lack the desired efficiency, others are difficult to control, and all have high operating costs. Little information is available on the biological degradation of cyanates. Thiocyanate pollution has a long history but its characteristics commonly are misunderstood or ignored; lower treatment efficiency follows. Since the three anions are related in chemistry, in industry, and in waste control, a group comparison should bring out certain aspects of the individuals that might otherwise be unnoticed.

Research in this laboratory[1] demonstrated surface water degradation of cyanide and associated wastes. Pettit and Mills[2] treated relatively high concentrations of cyanide on percolating filters. Other investigations by the same group followed[3,4] and more were in progress through 1959. Gurnham[5] reviewed British research for the Purdue Conference. Organisms associated with cyanide degradation were characterized in cited material and by Trelawney, et al.[6] Nesbitt, Kohl, and Wagner[7] studied activated sludge sustained on a mineral supplemented cyanide feed.

Chemical behavior of cyanates in water has been well documented. Acidity affects the rate of cyanate hydrolysis, which is rapid at pH 1.0 and negligible above pH 7.2. Resnick, Moore, and Ettinger[8] reviewed and rechecked pH effects on hydrolysis rates and studied the effect of biological degradation in surface water. Anaerobic action resulted in cyanate disappearance with ammonium formate as a likely first stage degradation product. Aerobic cyanate degradation[8] was not detectable in river water (pH 7.2) for ten days. A recheck during this investigation showed negligible cyanate degradation in river water for one month; two thirds was destroyed in another month. Added cyanate at 90 days was degraded slowly after a negligible lag.

Arthur Key[9] reviewed thiocyanate waste studies cited [10,11,12] and others. Both percolating filters and activated sludge caused thiocyanate degradation after acclimation. Test feeds generally consisted of a small percentage of gas works waste in sewage. Performance was affected by tar, phenol, and ammonia in the feed as much as by thiocyanate. Thiocyanate sulfur appeared in the effluent as ammonium sulfate. A high removal of SCN occurred in the top of a filter, whereas toxicity was evident at the start of activated sludge aeration. After complete treatment, both processes produced acceptable effluents. Badger and

Jackson[13] treated thiocyanate in spent gas liquor successfully by activated sludge with 1/1 recirculation of the effluent.

Key's observation[9] on the greater tolerance of filters for shock loads expressed a frequently accepted theme. It is more likely that differences between trickling filter and activated sludge processes are secondary as both share similar biosorption, growth, and oxidation characteristics. Cooke[14] reported a large variety and quantity of fungi in filter slimes. Performance differences may be associated with the relative activity of fungi and algae in process and to factors such as cell growth or frothing which affect each process differently.

Oxidation Methods

Continuous bench scale (complete mixing) activated sludge units[15] were used for testing each of the three chemical feeds in sewage. Information sought included behavior in response to the particular feed, load ratio, operating conditions and toxic effects. A respiration unit operating on a prescribed continuous feed schedule, revealing oxygen utilization, carbon dioxide and other volatiles in the recirculated air, occasionally was used to check behavior. Effects of slug doses, temperature, and the ability of an acclimated sludge to treat a different feed were studied.

Dosage was calculated on the CN basis in cyanide tests, OCN basis for cyanate and SCN for thiocyanate. Potassium or sodium salts showed no detectable differences when loading was based on the anions.

Degradation Pathways

The mechanics of biological degradation of the test chemicals are incompletely known; however, certain of the known products suggest possible pathways. Carbon, nitrogen, and sulfur are included in thiocyanate, hence it will be used as an example. This and earlier studies show formation of carbon dioxide, ammonia and its oxidation products, and sulfate from thiocyanate degradation. These products may be formed as follows:

1. $KSCN + 3H_2O \longrightarrow KOH + CO_2 + H_2S + NH_3$ — neglecting likely recombination.
2. $H_2S + 2O_2 \longrightarrow H_2SO_4$
3. $NH_3 + 2O_2 \longrightarrow HNO_3 + H_2O$

Equation (1) illustrates hydrolysis as a first stage reaction in which free oxygen is not required for carbon dioxide production. Cyanate exhibits a similar pattern but cyanide requires free oxygen for producing carbon dioxide. Ammonia

formation occurs early in degradation of each of the test chemicals but some authorities question its appearance as a first stage product.

Likely intermediates and free oxygen requirements for carbon, nitrogen, and sulfur degradation of each chemical are included in the following:

Feed ion (1 mole)	Moles O_2 for carbon oxidation	Moles O_2 for nitrification	Moles O_2 for sulfur oxidation	Likely first stage products	Total O_2, g O_2/g test ion
CN	1/2	2	none	KOH,CO_2,NH_3	3.1
OCN	none	2	none	KOH,CO_2,NH_3	1.5
SCN	none	2	2	KOH,CO_2,NH_3,H_2S	2.2

These data show nitrification as a major item in oxygen requirements for each chemical. Cell production represents assimilation of a major amount of carbon, therefore supplemental carbon may improve performance. Weak sewage gave some supplements but each chemical was tested with and without supplementary dextrose.

Analytical Procedures

Analytical determinations included cyanide(16,17) cyanate(8) and thiocyanate.(18) Early work established the absence of cyanide in thiocyanate effluents.

Nitrogen conversion, common in treatment of each of the test feeds, necessitated determination of ammonia, organic, nitrite, and nitrate nitrogen for performance evaluation. Sulfide and sulfate were checked in thiocyanate sludges. Cyanate effluents were tested for cyanide in case OCN reduction occurred. Additional determinations included effluent pH, suspended solids, and COD on 48-hour preserved composites. BOD tests(16) were based on fresh samples collected during the maximum load period. COD tests did not provide a good estimate of the three test chemicals because of hydrolysis, volatility, and ammonia behavior. Later data shows that effluents containing large amounts of OCN and SCN did not show proportionately high COD's.

Mixed liquor solids, sludge density index, percent volatility(16) and percent nitrogen, volatile solids basis, were determined weekly. These provided data on general sludge characteristics, gain or loss in solids, and mean daily load ratio, i.e., g BOD added/g mixed liquor volatile solids (MLVS). Influent oxygen demand included the sewage five-day BOD, total chemical demand and 1.0 g of BOD for each g of added dextrose where applicable. The resulting load ratio represented a compromise value generally higher than the effective loading.

Data Presentation

Data are reported as histogram pairs, one showing the percentage of sewage and test chemical nitrogen in the influent, while the other shows effluent ammonia, organic, and oxidized, (nitrite and nitrate) nitrogen as a percentage of total feed nitrogen. Nitrogen in removed sludge was included with the effluent bar to complete the nitrogen balance. Test chemical nitrogen in the effluent histogram represents supplementary data; it should not be included in the material balance because it would be partially or completely included as organic nitrogen. This method summarizes results as in a previous nitrile study[19] giving nitrogen recovery and percentage conversion.

The histograms include results over a prescribed period but do not indicate short time changes. These are shown by line graphs of pertinent parameters as a function of time, giving inter-relations with each other and with test conditions.

Two respiration test results are included as line graphs. These show oxygen utilization and carbon dioxide production versus time for a 24-hour period. Respiration tests were made with the same sludge and an identical but enclosed unit. Consequently, there was no break in observation continuity while measuring oxygen utilization and carbon dioxide, ammonia, hydrogen sulfide, or cyanide in recirculated air.

Cyanide Degradation

Data on nitrogen balances for four different periods in activated sludge treatment of cyanide and sewage are shown in Figure 1. Nos. 1 and 2 show acclimation with and without dextrose. Figures below the histogram pairs include CN influent concentration, supplementary feed, total applied nitrogen, load ratio range, prior sludge feed, and test interval.

Acclimation time for cyanide (No. 1, Figure 1) was relatively long for 5 mg/l CN without dextrose. Load ratio increases during the test were due primarily to MLVS losses amounting to about one-third of the initial solids. Nitrification was negligible for four weeks then increased rapidly. Effluent CN-N appeared during the first two weeks with negligible amounts thereafter. Feed CN removal in process was 99% during the test interval. Sludge behavior was typical of an underfed unit.

No. 2, Figure 1 illustrates acclimation with 10 mg/l CN feed in sewage with 2 g of added dextrose per day. During the three-week test with double the initial cyanide, a better material balance was evident with product distribution similar to No. 1. More effluent cyanide appeared during the first week but this decreased rapidly. Greater solids gains occurred with dextrose feeding, and treatment was more consistent. Results indicated that 2 grams of dextrose per day was excessive as shown by high load ratios and a slower buildup

in nitrification as compared with that using 1 g per day of dextrose. Supplementary energy materially shortened acclimation time, however.

Operation with 15, 25, and 35 mg/l CN with dextrose (No. 3, Figure 1) show excellent performance with acclimated sludge. Influent cyanide nitrogenwas about 40% while the effluent showed nearly 60% oxidized nitrogen. Cyanide removal was 99.8%. The nitrogen percentage as removed sludge show excess solids production while the smaller percentage in test 1, Figure 1 was due to analytical removal.

No. 4, Figure 1 shows the results of 40 and 50 mg/l CN feeding. A feed containing 60% CN-N resulted in an effluent with more than 50% oxidized nitrogen. Process removal of CN was 98.4% with slightly less nitrification. Effluent ammonia nitrogen, like cyanide nitrogen, generally increased for a short time after each dosage increase. Results include the period of adjustment to the new dosage which exaggerates effluent CN.

Histogram pairs Nos. 5 and 7, Figure 2 show questionable performance on similar but separate sludges differing primarily in adjustment time allowed between dosage increases. No. 5 at 45 mg/l feed CN shows high effluent ammonia, low oxidized nitrogen (primarily nitrite) and a poor material balance. Adjustment time between dosage increases was two weeks. No. 7 shows more pronounced effects on 75 mg/l CN dosage although effluent nitrite remained low. Three-week adjustment periods between dosage increases were used. The higher loading before difficulty occurred, and the good performance at 60 mg/l CN (No. 6) shows that longer adjustment time was beneficial. No. 7 test wasthe first to show significant aeration loss of cyanide (14 and 18 percent). This alone would discourage activated sludge treatment of cyanide at this feed concentration and mixed liquor solids level. Both units were still functioning as shown by at least 90% destruction of cyanide retained by the sludge but were rejected because of one or more objectionable features. Subsequent data will clarify these relations.

Histogram pair No. 8, Figure 2 shows nitrogen behavior under conditions more likely to be found in practice. Dosage was varied daily between 10 and 75 mg/l CN by random selection of a card. The sludge had been dosed with 75 mg/l CN during the previous week to observe effects of a random load after an over-dose. This factor and inclusion of the overload in the random feed provided information on sludge recovery and variable loading.

Influent CN-N of 60% (No. 8, Figure 2) resulted in an effluent with 40% ammonia and 20% oxidized nitrogen. Process CN removal exceeded 99%, part of it as aeration loss during two 75 mg/l CN feeds. Most of the oxidized nitrogen (19 of 22 percent) appeared during the last two weeks, which shows improving performance on the variable load.

British research[20] also encountered CN loss by volatilization. An uninoculated filter resulted in 66% loss of feed cyanide

with no evidence of biological action. Seeding with acclimated organisms from activated sludge resulted in good conversion of cyanide to ammonia after one week in the same filter. Matured filters also showed volatilization loss of cyanide at higher dosages. Ammonia and oxidized nitrogen in the effluent represented only 70% of the feed cyanide nitrogen at 68 mg/l dosage. Percolating filters[21] did not result in cyanide-free effluents at dosage of 88 mg/l or above. "Activated sludge bench tests[22] operating at about 50,000 mg/l of mixed liquor solids showed good conversion of cyanide to ammonia at feed levels of 60 to 180 mg/l as HCN. Nitrification was negligible above 60 mg/l CN. Aeration losses were negligible at the high solids level but performance was less encouraging at 4000 mg/l of mixed liquor solids.

British results[23] show that about 0.6 lbs. of HCN/cubic yard/day can be treated by percolating filters. This yields an effluent containing less than 1 mg/l of cyanide with operation temperatures of at least 10°C, influent concentrations of 60 mg/l or less as HCN, and a supplementary nutrient, such as peptone, in the feed.

Direct comparisons between activated sludge and trickling filter performance are difficult but it is apparent that behavior changes in both above about 60 mg/l feed CN. About 0.1 lb. of CN/lb. of MLVS/day was treated by activated sludge with results comparable to those of No. 6, Figure 2. This was achieved at 1100 to 1500 mg/l of MLVS.

Cyanide Sludge Performance Variation

Cumulative results as in Figures 1 and 2 fail to show performance changes; the line graphs in Figure 3 serve this purpose. Important performance parameters are plotted in 48-hour intervals against time in days. The missing days in the abcissa are the result of feeding five days per week and resting the sludge on week-ends.

Figure 3 shows a sludge after dosage was increased from 35 to 45 mg/l CN. Percent cyanide removal dropped during the second week and recovered in the third week. COD removal did not recover in the same interval, but effluent suspended solids did. Effluent ammonia nitrogen rose after the fourth day with oxidized nitrogen showing a slow recovery after the tenth day. The sludge was still doing a fair part of its intended work although definitely substandard (cf No. 5, Figure 2).

Figure 4 illustrates the performance of a sludge that had been allowed a three-week adjustment period between dosage increases (No. 6, Figure 2). The sludge had been operating on 50 mg/l CN prior to this test. Similar fall-off in performance was evident, as in Figure 3, but each applied test showed that at different time intervals performance recovered to that observed initially. The importance of a three-week period between dosage increases is apparent from Figure 4. Had a feed increase occurred at the end of two weeks,

nitrification interference would have carried over to the new dosage. Apparently other factors behaved similarly, as the sludge allowed two weeks between cyanide increases was sick at 45 mg/l CN whereas this one performed satisfactorily at 60 mg/l. Percent BOD removal afforded little information on cyanide sludge condition, as it held between 94 and 97 percent while other tests showed significant variation. Performance in Figure 4 was similar to that during acclimation of a new sludge; graphs on acclimation, therefore, were omitted.

Figure 5 shows the trends on the same sludge presented in No. 7, Figure 2. Percent BOD removal on cyanide sludge was misleading as the results show a ficticious improvement. BOD tests were equally misleading in cyanate and thiocyanate trials.

Percent CN removal (Figure 5) decreased in an irregular manner. COD removal varied around 80%. Effluent suspended solids indicated fair performance but nitrification dropped rapidly and stayed down. Aeration loss of cyanide was evident by odor throughout the test interval. Poor recovery of feed nitrogen is attributable to both cyanide and ammonia aeration losses.

Line graphs on random cyanide dosage are shown in Figure 6. As described earlier (test 8, Figure 2) this sludge was below par in initial performance.

Cyanide removal was above 90% on all but two samples. COD removal improved and generally held above 80%. Effluent solids decreased rapidly. Nitrification was low during the first two weeks then gradually improved. In spite of a dosage range from 10 to 75 mg/l CN a sick sludge showed good recovery from variable loads but performance was inferior to that on steady dosage. The line graphs show that long term testing and more than one test parameter are necessary to evaluate performance on problem wastes.

Respiration Tests

Figure 7 shows the response of a cyanide feed in sludge respiration during the acclimation period. Test 1 was made on the sludge considered in histogram 1, Figure 1, after four weeks' operation; test 2 during the sixth week.

Observations were made at frequent intervals during the first seven hours; the next five hours and the last twelve hours were grouped and a mean reported. Data for 16 hours are reported in Figure 7; that after 12 hours indicates the general level of respiration following the feed. The mixed liquor was operated for 24 hours at 30°C in the enclosed unit prior to respiration tests. Three-fourths of the daily feed was added in six hours and the remainder by twelve hours to exaggerate shock loads in respiration tests.

Pronounced inhibition is shown for curve A (oxygen utilization) and curve B (carbon dioxide) in test 1. As the feed rate

decreased after six hours both curves showed increased respiration. The data shows that this sludge, after four weeks' acclimation, was unable to cope with a shock load. Curves C (O_2) and D (CO_2) show different behavior during the sixth week. The same rapid feed rate resulted in a prompt rise in both curves with curve D peaking slightly earlier.

Subsequent tests on cyanide, cyanate and thiocyanate sludges are not presented as toxicity was not as definite. A new cyanate sludge did not result in early depression of the curves but the rise was not significant either. Thiocyanate toxic effects were mild for a few days. Both cyanate and thiocyanate sludges showed improved acclimation mainly by an increased slope during the period of rapid feeding.

Slight lags occurred before respiration increased on rapid feeding of an increased chemical dosage. Oxygen utilization varied with nitrification rate, while the carbondioxide curves showed a minor lag with dosage changes and less evidence of toxicity.

Aeration losses of cyanide at or below 540 mg of cyanide per 24 hours under respirator conditions rarely showed as much as 1 mg trapped from recirculated air. At 675 mg CN (75 mg/l) two separate tests showed 97 and 123 mg of CN per 24-hours recovered from the air. The sludge apparently was capable of holding the cyanide until hydrolysis occurred at the lower dosage level. At the highest test dosage retention capacity was exceeded. MLVS test range was 1100 to 1500 mg/l which limits data on cyanide aeration losses vs. solids level. British research[22] showed that higher solids decreased aeration losses.

Cyanide determination in the mixed liquor during a respirator test after 330 of a 405 mg CN feed had been introduced showed 17.6 mg of CN in the unit (no effluent CN). This shows destruction of 312 of the 330 mg of applied CN or 95% of that fed within six hours. It is evident that CN destruction is relatively rapid whereas nitrification and sludge regeneration occurs more slowly. High feed rates during respiration tests generally resulted in decreased nitrification.

Similar tests on SCN indicated a like pattern with five times the feed concentration. Thiocyanate treatment usually allowed some breakthrough to the effluent whereas CN showed none except during acclimation, after significant load increases or overloads.

Cyanate degradation rate was lower; 10 to 50 percent of the feed OCN appeared in the effluent during respiration tests. High feed rates significantly reduced performance.

Losses of ammonia by aeration were relatively low and followed a pattern similar to that of nitrile sludges[19] i.e., ammonia losses

were significant at a pH above 7.8 and ammonia level above 30 mg/l. Cyanide sludges usually had a pH of 7.8 to 8.1 but high ammonia occurred mainly during the adjustment period or at high loading. Thiocyanate sludges maintained a pH of 6.7 to 7.5; hence, they retained ammonia in spite of high mixed liquor concentrations. Cyanate units had a pH of 8.0 to 8.3 but nitrification normally prevented ammonia accumulation. High sludge buffer capacity maintained a high pH in spite of nitrate production but sulfate production contributed to a lower pH.

Thiocyanate Degradation

Thiocyanate cumulative behavior is presented in Figure 8. No. 9 shows the nitrogen balance for acclimation without supplementary dextrose, No. 10 with it.

The increased load ratio for No. 9 is partially due to a feed increase of 10 to 40 mg/l SCN, but mainly to MLVS losses. After three weeks of acclimation, SCN removal was good but nitrification was just beginning. No. 10 operated on a higher load of SCN from the start. Effluent SCN was higher during the first week but acclimation and nitrification occurred earlier. Both units showed high effluent organic nitrogen during acclimation. The 2 g of dextrose per day contributed to high load ratios; acclimation probably would have been more rapid at a lower dextrose feed.

Dosage of 40 to 160 mg/l SCN (feed doubled twice in seven weeks) provided the nitrogen data in No. 11, Figure 8. Greater proportions of effluent nitrogen appeared as ammonia at higher SCN feeds. Nitrification was very good at 80 mg/l SCN but a decrease at 160 resulted in a lower mean in summary data. Low organic nitrogen and good SCN removal were characteristic of acclimated SCN effluents.

Results of high SCN dosage with and without dextrose are shown in Nos. 12 and 13, Figure 9. Both histogram pairs show further evidence of nitrification difficulty at high SCN feed levels. No. 12 sludge, with dextrose, showed evidence of septicity in local sludge agglomerates indicating insufficient oxygenation. A temporary upset occurred in the sludge when dextrose feeding was omitted. This was accompanied by sludge solids destruction and concurrent high load ratios. The sludge was gaining solids by the third week but did not recover to the initial solids level by the fifth week. SCN removal with and without dextrose was similar (96 and 98 percent) showing that supplementary energy wasn't needed at this feed level and that the higher load ratio did not affect SCN removal.

The test on random dosage changed daily from 50 to 400 mg/l SCN (No. 14, Figure 9) was remarkably similar in results to tests 12 and 13. Dosages above 300 mg/l SCN were drawn more than 75% of the time.

More detailed information on random SCN loading is shown in the line graphs (Figure 10). Percent SCN removal varied from 90 to 99 in an irregular manner that could not be associated with influent SCN levels. COD removal and effluent solids were exceptionally good. Effluent ammonia nitrogen remained high but nitrification was evident throughout the test period.

SCN toxicity was not observed in an acclimated sludge as indicated by earlier observations.(9) There was no evidence of high nitrites in the effluent as reported by Key.(9) Difficulty in destroying SCN, as encountered by Badger and Jackson,(13) Potter and Hunt,(24) Catchpole,(25) and others in tests using spent gas liquor feeds, did not appear. Catchpole(25) reported that ammonium chloride, ammonium thiosulfate, phenol, catechol, and other substances in spent gas liquor inhibited oxidation of SCN. This has given rise to two-stage treatment in which SCN is oxidized after the inhibitory substances are reduced to levels acceptable to SCN-consuming organisms. Catchpole feels that this could be handled in a single unit with appropriate allowance for oxidation time. This investigation did not include effects of inhibitory substances.

Hydrogen sulfide was never detectable in amounts exceeding analytical error in mixed liquor, recirculated air or effluents during this study. If sulfide formed it must have been rapidly oxidized. SCN-S was recovered in the effluent as sulfate in amounts ranging from 88 to 95 percent.

The oxygen demand load in SCN feeds, therefore, included at least two oxidation rates, i.e., a high rate for sulfur oxidation and a lower rate nitrification. The greater proportion of nitrification with low SCN feed levels than with high SCN feeds suggests preferential sulfur oxidation and insufficient oxygenation at high loads.

Cyanate Degradation

Figure 11 shows the cumulative nitrogen balances for cyanate-fed activated sludge. No. 15 shows acclimation to 50 mg/l OCN during a three-week period. Cumulative results show 55% OCN removal; first week removal was lower. Dextrose addition of 2 g/day was decreased to 1 g/day during the third week, which accounts for the load ratio changes. An earlier acclimation test achieved 80% OCN degradation by the end of three weeks at 50 mg/l OCN feed; higher degradation was not obtained consistently during extended operation. Daily results ranged from 65 to 90 percent OCN removal at normal dosage, for undetermined reasons. Sludge acclimation to cyanate without supplementary dextrose resulted in about 50% loss in mixed liquor solids within two weeks. OCN degradation started to improve, then fell off with decreased solids. Dextrose feeding at 1 g/day resulted in unit solids increases, but OCN degradation did not approach the 80% level until MLVS reached about 1500 mg/l.

Doubling MLVS did not improve OCN degradation. The cumulative results in No. 15, Figure 11 were obtained at 1200 to 1400 mg/l MLVS; hence, this probably accounts for the lower OCN removal as compared with earlier acclimation tests.

No. 16, Figure 11 shows effects of increasing aeration from 12 to 24 hours in an attempt to improve treatment. Mean OCN removal was 84%. Nitrification was exceptionally good. The gain due to doubled aeration time was not considered economically justifiable.

No. 17, Figure 11 shows behavior when the sludge was forced to use OCN nitrogen as a source of ammonia. Sewage was inadvertently added on the first and last days of the test, otherwise influent nitrogen was included as cyanate only with more dextrose to increase metabolic nitrogen requirements. Much higher effluent organic nitrogen and 71% OCN removal show that this approach was unsuccessful.

A third modification to assist OCN degradation provided results in No. 18, Figure 11 where mixed liquor pH was reduced by sequential use of a phosphate buffer or ferric chloride in the feed and carbon dioxide added with the air. The buffer and ferric chloride failed to decrease pH below 7.5. Carbon dioxide reduced mixed liquor pH to about 6.0 during introduction. CO_2 feed problems resulted in irregular flow but the cited pH was maintained generally.

OCN degradation of 93% for the test period and 97% during the three weeks of carbon dioxide use show a major improvement. At the lower pH, both chemical and enzymatic hydrolysis of OCN were possible. Effluent suspended solids increased because the mixed liquor was supersaturated with CO_2, some of which was released in the settler and raised solids with it. Flocculation and nitrification deteriorated during carbon dioxide use. Results indicate that pH reduction prior to the aeration step would be preferable. Carbon dioxide, flue gas or mineral acids should be effective.

Random dosage of OCN between 50 and 400 mg/l (No. 19) showed less effective performance than for similar tests on CN or SCN. About 71% OCN degradation occurred in this interval.

Figure 12 shows line-graphed data on the variable cyanate load described in No. 19, Figure 11; decreased cyanate removal shows clearly. COD removal was variable but fairly good. High effluent solids were commonly encountered; effluent oxidized nitrgen rapidly decreased during the second week. Sludge deterioration near the end of the test gave further evidence of decreased efficiency.

Cyanate breakdown of about 80% was easily attained but biological resistance of the remaining fraction was unusually

high. Mixed liquor pH reduction was the only means tried that improved degradation. Hydrolysis of the cyanate ion appeared to be the controlling factor but the usual means of forcing equilibrium were unsuccessful.

Cyanate sludge was relatively inconsistent. The floc was unusual in that it generally consisted of granules connected by short filaments. The filaments had some effect on sludge compaction and clarification.

Cyanide was found in a cyanate effluent only once in six months. Influent sewage at pH 3.5 resulted in an effluent with 0.06 mg/l CN. This amount of cyanide may have been the result of contamination or interference. It is not likely that influents often will have a pH in this range, hence significance of this value is reduced. Relatively little sludge disturbance was encountered due to vagaries of the influent sewage in CN and SCN operation.

Nitrite Production

Nitrite production was different in cyanide, thiocyanate and cyanate sludges. High nitrites appeared in cyanide sludge following a dosage change. If NO_2-N exceeded 15 to 20 mg/l for more than three or four days the nitrite upset the sludge more than the cyanide and significantly reduced performance.

High nitrites were rare in thiocyanate sludge but were frequent in cyanate sludge. Similar quantities of nitrite and nitrate nitrogen were commonly found in cyanate effluents. During one 16-day period effluent nitrite ranged from 25 to 36 mg/l with a nitrate range of 15 to 27 mg/l. This may have contributed to treatment variability but the connection was indefinite. No explanation was found for the apparent tolerance of cyanate sludge for nitrites while the cyanide sludge was noticeably inhibited by nitrites.

Low Temperature Operation

Previously described data generally were obtained in operation at 22 to 25°C. Acclimated sludge for each chemical was operated at 5°C for four weeks then returned to room temperature to observe the effects of low temperatures and the change. Dosage during this series was 30 mg/l for CN and 100 mg/l for OCN and SCN or about one-half of that readily treatable at room temperature. Feeding 1 g of dextrose per day was continued.

Cyanide removal at 5° promptly decreased to a low of 55% then recovered after the first week to a range of 70 to 95 percent. COD removal stayed down to 20 to 40 percent while at 5°.

Continuous MLVS losses amounted to about one-half of the initial solids after four weeks. It is likely that cyanide removal would decrease further at some undetermined low solids level. Good performance, except nitrification, was regained in about three weeks of room-temperature operation.

Cyanate removal at 5° reached a low of 19% in the first week; it recovered to about 40% during the second week and 60% thereafter. COD removal decreased to 40% during the first week with a range of 55 to 80% in the next three weeks. A temporary loss in unit solids was followed by a gradual gain. Low temperature operation on cyanate evidently could have continued indefinitely at reduced efficiency. Readjustment to room temperature operation was a matter of hours as performance following the change was equal to or better than normal.

Thiocyanate removal at 5° decreased to 27% during the first week with recovery to about 75% for the remaining test interval. COD removal decreased to 55% and recovered to about 75% during the same interval. Unit solids gain were small but consistent with low effluent solids excepting the first two days at 5°. The unit gave evidence of continued treatment at reduced efficiency in low temperature operation. Performance was normal within two days at room temperature operation.

Although cyanide sludge achieved fair cyanide degradation at 5°, poor assimilation and inability to maintain unit solids indicated eventual failure. OCN and SCN sludge showed better low temperature tolerance but lost a significant fraction of their efficiency. Nitrification was low on all sludges at 5° and recovered more slowly than other performance factors after increasing operation temperature.

These results and those of a previous study[27] demonstrate the desirability of the use of heat and/or enclosures to protect biological treatment units from low temperatures when treatment efficiency is critical.

Slug Dose Tests

Occasional dosage of a given chemical may have significant effects on biological treatment when the same dosage may be easily metabolized in an acclimated system. Each chemical therefore, was applied in addition to a maintenance feed to an unacclimated sludge during one 24-hour period. Performance was followed for three weeks after the slug dose to observe maximum effects and recovery. The maintenance feed consisted of sewage, gelatin and fish meal at a daily load ratio of about 0.4 g BOD per g MLVS. Slug doses were 90 mg as CN^-, or 450 mg of OCN^-, or SCN^- (10 and 50 mg/l respectively).

Effluent cyanide was not detectable after the slug but cyanide odor was perceptible over the aerator during the feed. COD removal decreased to 75% for two days then recovered to a normal range of 85 to 91 percent. Effluent solids raised to 60 mg/l for the same two-day period then returned to normal. Unit solids gains were low during the first and second week. Nitrate production was low on the third and fourth day then returned to a normal range of about 20 mg/l by the fifth day. Apparently the cyanide was bacteriostatic to nitrifiers rather than toxic.

About 70% of the thiocyanate was recovered in the effluent within two days. COD removals were unaffected by the slug dose. A slight increase in effluent solids occurred during the second week after SCN dosage but this may have been normal variation. Nitrification and unit solids behavior were not significantly changed.

Cyanate slug dosage resulted in recovery of 485 mg of effluent OCN within four days. The excess over the intended 450 mg dosage (8%) may have been the result of dosage error or analytical error. Cyanate analysis of control, CN or SCN sludge effluents showed from 0 to 5 mg/l as OCN. This apparently was due to incomplete separation of interference in the cation exchange column used for this purpose. Low interference was obtained only when the column was regenerated to the hydrogen form then converted to the sodium form for use. Time limitations occasionally resulted in use after one regeneration, as for this series. This contributed to higher recovery but would not account for the 8% excess. Dosage error probably was involved. Nevertheless, it is apparent that OCN degradation or hold-up was negligible following the slug dose. COD removals were affected by 75 mg/l of effluent solids during the first two days then both recovered to normal ranges. Nitrification was unaffected but unit solids gains were low during the first week.

SCN and OCN slug dosage had minor effects on treatment of the maintenance feed except for solids relations; these recovered quickly. Conversely the sludge had little effect on either of the chemicals. Cyanide slug dosage had a much more pronounced effect but recovery was rapid. It also was destroyed in process. Acclimation studies reported earlier showed some degradation of all three chemicals within one week in new activated sludges. Significant degradation occurred only for cyanide in slug dosage. However, the results indicate that the effect of these chemicals on over-all performance of activated sludge is greatly over-rated. Failure is more likely to be due to a sick sludge during the slug dose or to other undetermined complicating factors. Subsequent to these tests a new sludge was dosed with 450 mg of CN in one day's feeding. Performance was definitely jolted for the first two days but showed evidence of recovery by the third day. Eighty-eight percent of the cyanide was removed.

Cross Acclimation

Youatt[26] and others postulated that cyanate was an hydrolysis product of thiocyanate. Numerous reports show cyanate as a first stage product of alkaline chlorination of cyanide, which implies similar behavior in biological oxidation. If this occurs, cyanate degradation would be common in treatment of the three tested feeds. Moreover, a sludge acclimated to one feed should readily adjust to the remaining two.

Tests were made to evaluate cross acclimation, or the ease of adjustment of an acclimated sludge to another feed. Each of the possible changes were tested including one in which cyanate and sulfur were fed to an SCN sludge. Youatt indicated sulfur oxidation in his cultures.

Dosage for cross-acclimation tests at room temperature was 30 mg/l for CN and 100 mg/l for OCN and SCN. This dosage was higher than for acclimation but did not eliminate this possibility.

Sludge showing cross acclimation from one feed to another would be likely to show negligible performance decrease from normal following the change. Enzyme adaptation may be required for metabolism of the new feed but if the existing population can produce the necessary enzymes, adaptation should be rapid. Continuous feed schedules required about one volumetric displacement of the aerator contents (12 hours) to achieve maximum concentration of the new feed in the mixed liquor. Enzyme adaptation should be complete in this interval. More time would be required for an adaptation including a new selection and build-up of tolerant organisms or mutation of existing strains. This would be considered reacclimation and would be associated with a significant performance drop followed by performance recovery.

Cross acclimation tests on nitrile sludges[19] were accepted if the new feed was treated successfully within one week with minor adjustment problems during the first week and good performance thereafter. Cyanide, cyanate and thiocyanate cross acclimation was more difficult to evaluate, as some tests showed good adjustment while others showed appreciable change. Judgment had to be based on over-all performance using several rating parameters. Table 1, therefore, includes performance according to several rating factors for three weeks following the feed change.

Over-all performance following the feed change shows more reacclimation than cross acclimation. None of the sludges satisfied the acceptance criteria for cross acclimation of nitriles.[19] Conclusions would be different if COD or chemical removal were accepted as the main considerations. Items 6 and 7 (Table 1) show initial cross acclimation but good performance did not continue through the test interval. Sulfur was not oxidized in item 7. Data on net solids change per g of influent BOD shows a wide range

during the observed period. This shows that the feed was not consistently converted to unit solids following the feed change. The lower gains or larger losses invariably occurred during the first week. Cross acclimation would have materially reduced these variations. This data does not indicate a common metabolic pathway for the three chemicals.

Summary

Data presented show that cyanate was more difficult to treat biologically than cyanide or thiocyanate. It would be unlikely to obtain the high treatment efficiency observed for both cyanide and thiocyanate if a cyanate intermediate was formed. Cross acclimation tests likewise did not indicate a common pathway. Therefore, degradation through the cyanate stage is incompatible with observed behavior.

Each of the test feeds resulted in activated sludges with individual characteristics. Organisms, response to control variables, acclimation, loading and efficiency were different for each feed chemical. Ammonia was a common degradation intermediate but its rate of appearance and susceptibility to nitrification in treatment varied with the test chemical. Many factors are involved in performance comparisons such as chemical removal, COD removal, acceptable concentration or load ratio, solids retention, oxidation, percentage and rate of removal, etc. More differences than similarities were encountered in such comparisons. However, each of the feeds was biologically treatable.

Conclusions

1. Cyanide, cyanate and thiocyanate are effectively degraded by activated sludge after two to three weeks of acclimation.

2. An additional source of metabolic energy, such as dextrose in the feed hastens acclimation to the three feeds and improves subsequent operation on cyanide and cyanate.

3. Activated sludge treatment of cyanide is less effective above a feed concentration of about 60 mg/l CN; cyanide removal percentage and nitrification decrease while cyanide stripping by aeration increases.

4. Adjustment periods between cyanide increases during acclimation affected sludge performance. Variable loads for an acclimated sludge had a small but noticeable effect on performance.

5. Thiocyanate sludges acclimated more rapidly and accepted loading up to the limit imposed by oxygenation capacity.

6. Nitrification by thiocyanate sludges occurred readily but showed decreased proportions of oxidized N at higher SCN loading.

7. Cyanate sludges approximated 80% OCN degradation as long as MLVS exceeded 1500 mg/l. A significant increase in degradation was achieved by lowering the pH to encourage chemical hydrolysis.

8. Cyanate sludges were unstable and were affected by changes in conditions or loading that were acceptable to CN or SCN sludges.

9. High nitrite formation was common in OCN sludges but the biota appeared more tolerant to nitrites than the CN sludge.

10. Low temperature operation of cyanide sludge resulted in lowered efficiency and probably eventual failure. Cyanate and thiocyanate sludges probably could have continued low temperature operation at reduced efficiency.

11. Cross acclimation and other comparisons of the three systems showed more differences than smiliarities in biota, performance, and response to control variables. It is not likely that cyanate is common to biological degradation of CN, OCN, and SCN.

12. Slug dosage of cyanide temporarily disrupted performance with degradation of the cyanide. Cyanate and thiocyanate slug dosage largely passed through the sludge with little effect on treatment of the maintenance feed. Sludge recovery was rapid for each.

13. Low temperature operation of biological processes should be avoided by use of heat or enclosures when treatment efficiency is critical.

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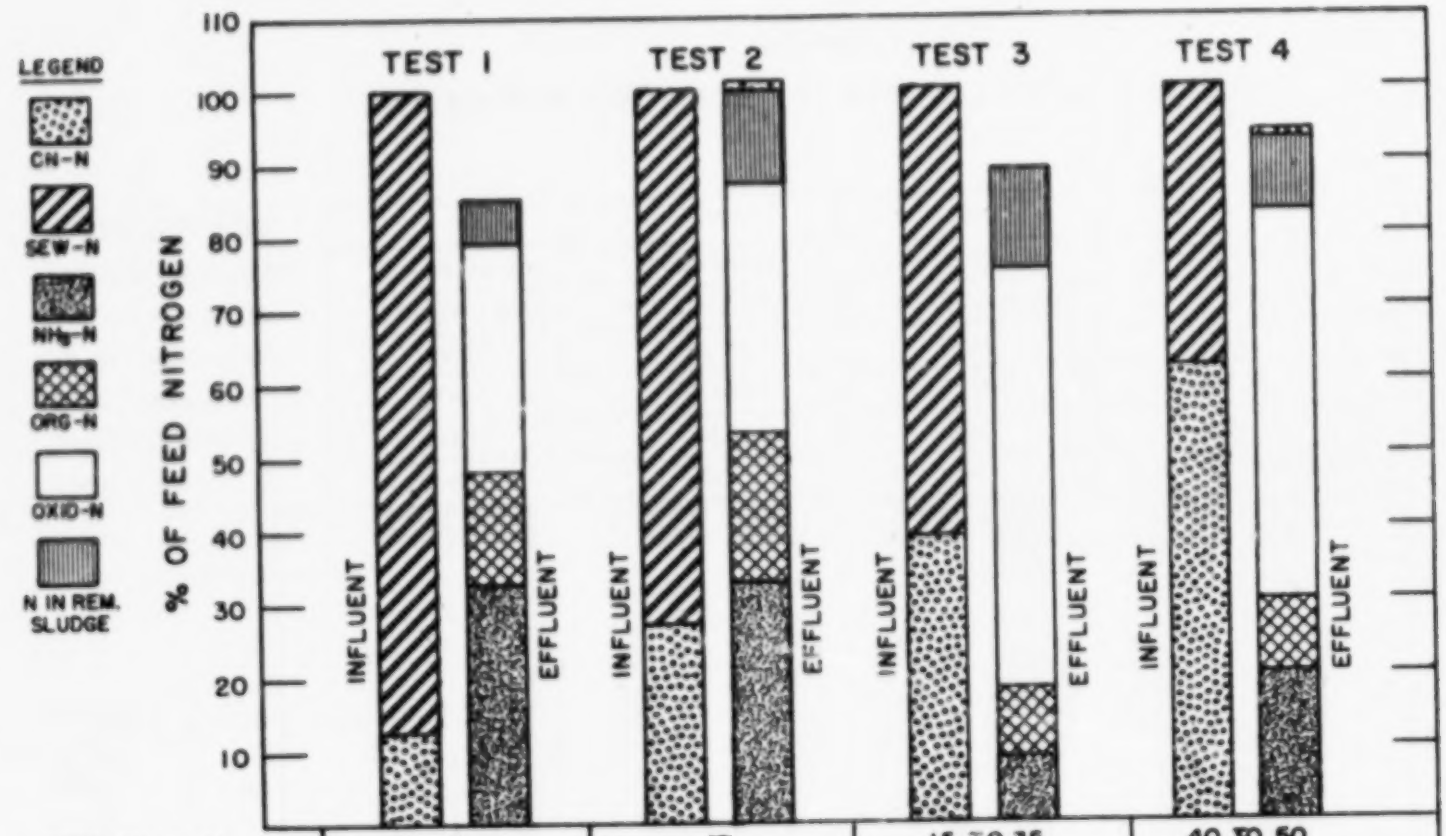
TABLE 1

ACTIVATED SLUDGE PERFORMANCE
AFTER A FEED CHANGE

Sludge Accl. To	New Sludge Feed	Recovery Time Chemical Removal	Recovery Time COD Removal	Nitrification	g Unit V.S. Per. g BOD FED	Remarks
1. CN^-	OCN^-	More than 21 days	Little change	Low - 21 days	-0.09 to 0.21	OCN^- removal 20 to 45 percent.
2. CN^-	SCN^-	6 days	6 days	Low - 4 days See remarks	-0.03 to 0.17	Low of 15% SCN^- removal @ 4 days High nitrite formation for 3 weeks.
3. OCN	CN^-	10 days	8 days	Low - 21 days	-0.01 to 0.24	Mostly nitrite N in the oxidized fraction.
4. OCN^-	SCN^-	10 days	8 days	Decreased after 4 days	0.03 to 0.10	Negligible SCN^- removal 3rd and 4th day.
5. SCN^-	CN^-	2 days	8 days	Low - 21 days	-0.12 to 0.21	Mostly nitrite nitrogen in oxidized fraction.
6. SCN^-	OCN^-	16 days	Little change	Low - 4 days	0.03 to 0.17	Good OCN removal 1st and 3rd week.
7. SCN	OCN + S	Decreased after 2 weeks	Little change	Low - 4 days	0.03 to 0.17*	Vol. solids N decreased from 9.2 to 4.4 percent. Negligible S. oxid.

* Solids gain was corrected by subtraction of the weight of added sulfur.



	TEST 1	TEST 2	TEST 3	TEST 4
FEED CN mg/l	5	10	15 TO 35	40 TO 50
SUPPL. SEWAGE (s)	YES	YES	YES	YES
SUPPL. DEXTROSE (D)	NO	2g/DAY	1g/DAY	1g/DAY
TOTAL INFL. N. mg	5930	3620	8950	10700
DAILY LOAD RATIO	0.07 TO 0.21/1.0	0.35 TO 0.56/1.0	0.29 TO 0.37/1.0	0.41 TO 0.55/1.0
PRIOR SLUDGE FEED	S	S	S+D+10 CN	S+D+30 CN
WEEKS OBSERVED	6	3	6	6

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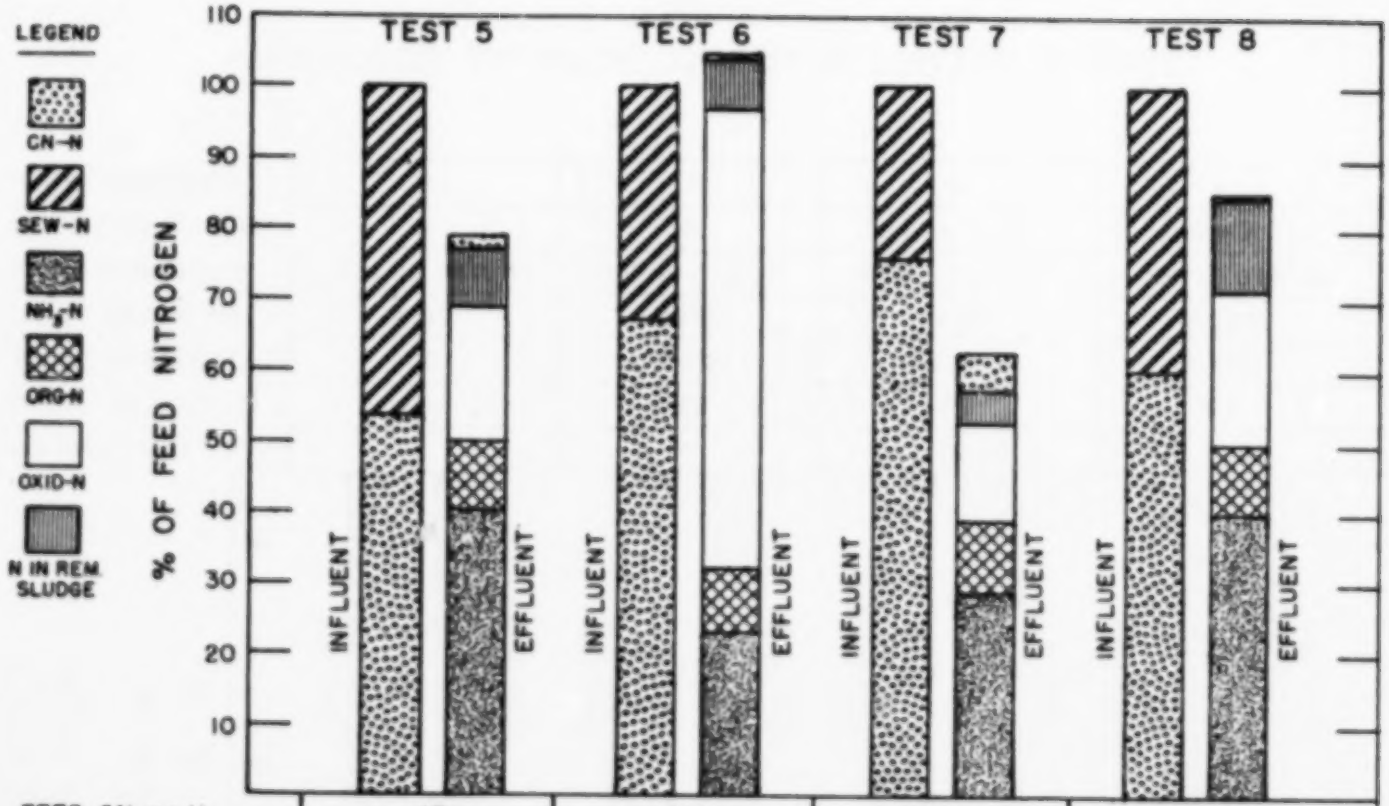
NITROGEN BALANCE ON KCN ACTIVATED SLUDGE

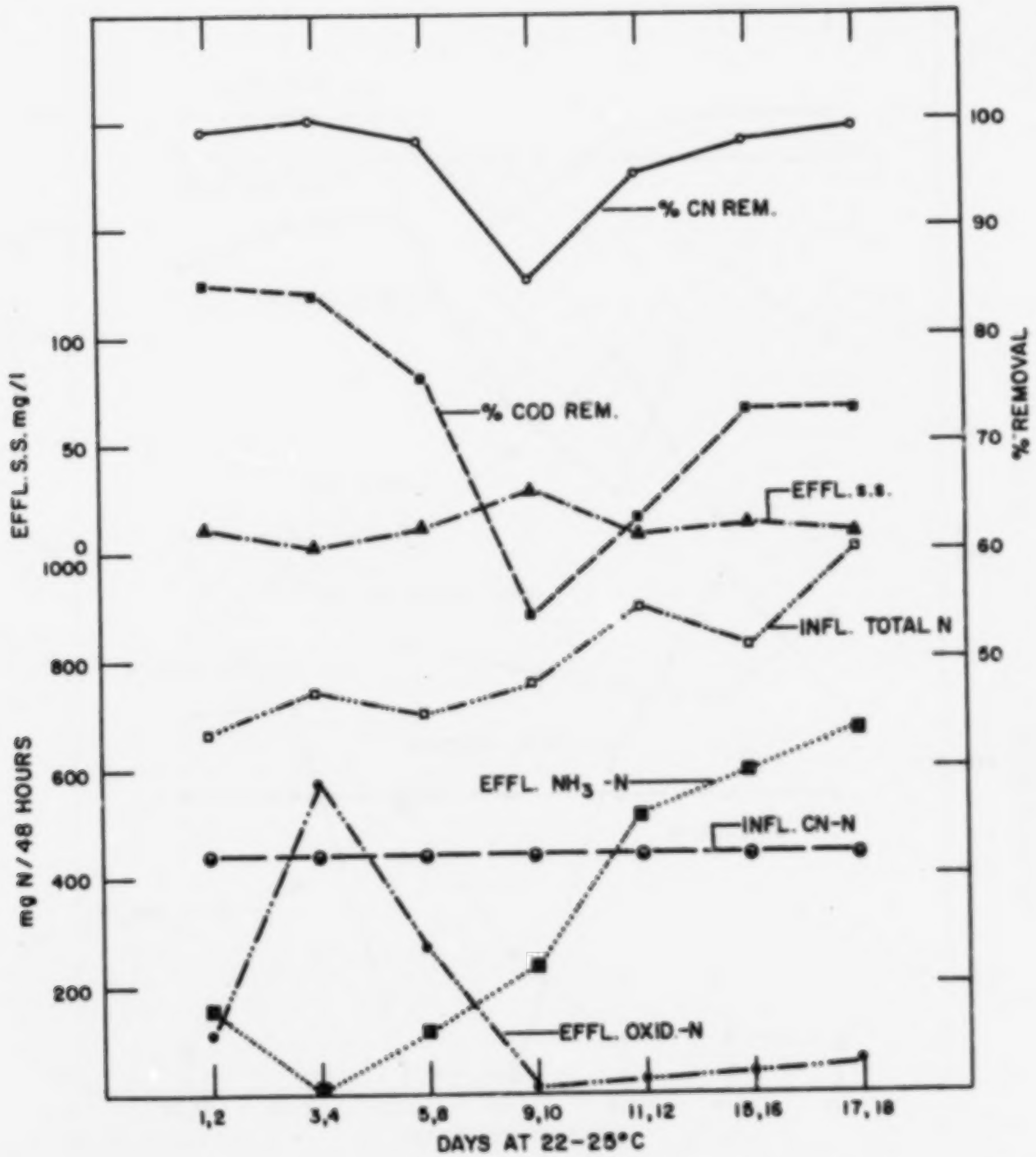
FIGURE 1



FEED CN mg/l	45	60	75	10 TO 75 VARIED DAILY
SUPPL. SEWAGE (s)	YES	YES	YES	YES
SUPPL. DEXTROSE (D)	1g/DAY	1g/DAY	1 g/DAY	1 g/DAY
TOTAL INFL. N. mg	5660	6730	7670	6910
DAILY LOAD RATIO	0.32 TO 0.38/1.0	0.46 TO 0.55/1.0	0.57 TO 0.61/1.0	0.31 TO 0.54/1.0
PRIOR SLUDGE FEED	S+D+35 CN	S+D+50 CN	S+D+60 CN	S+D+75 CN
WEEKS OBSERVED	3	3	3	4

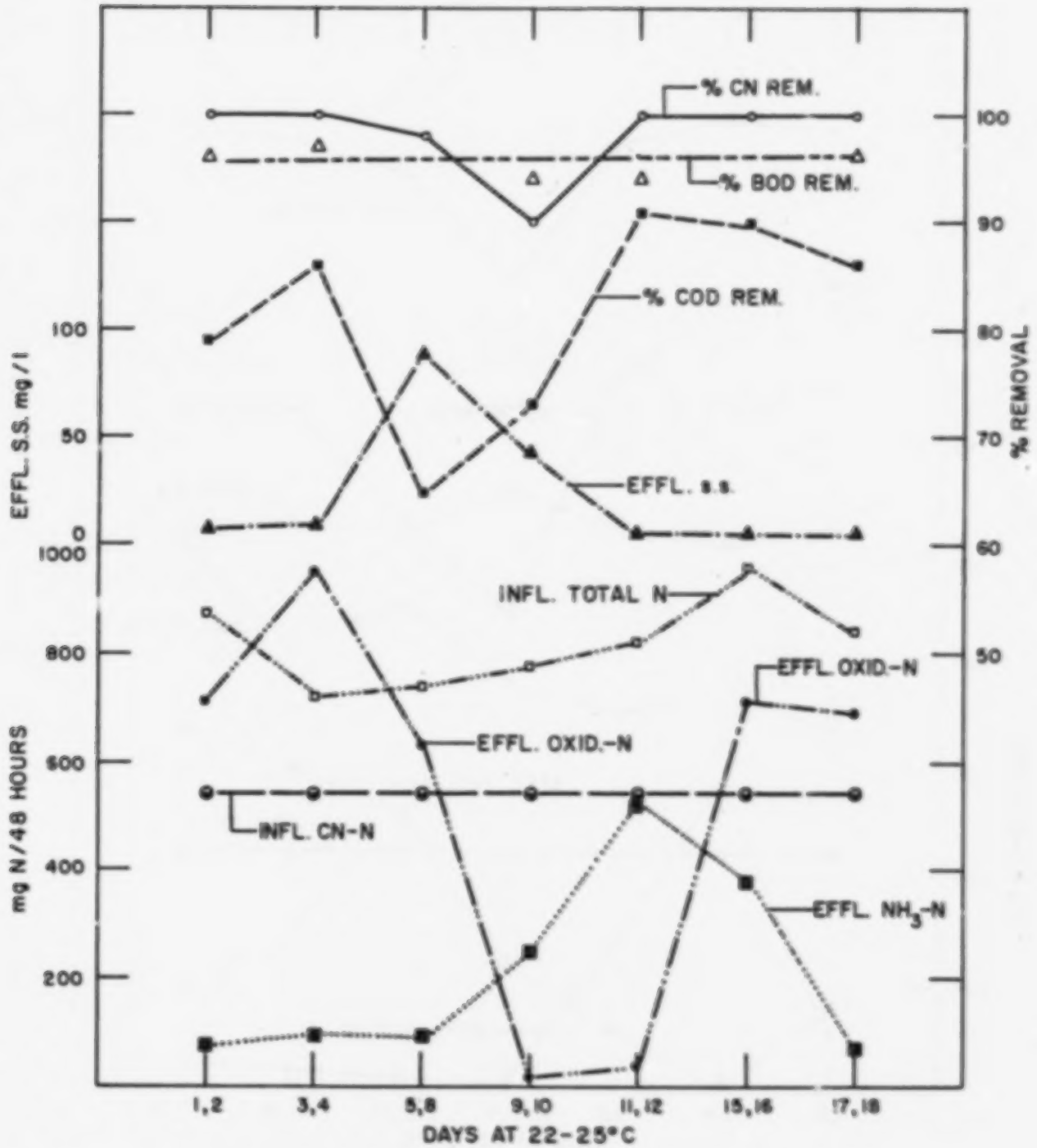
NITROGEN BALANCE ON KCN ACTIVATED SLUDGE

FIGURE 2



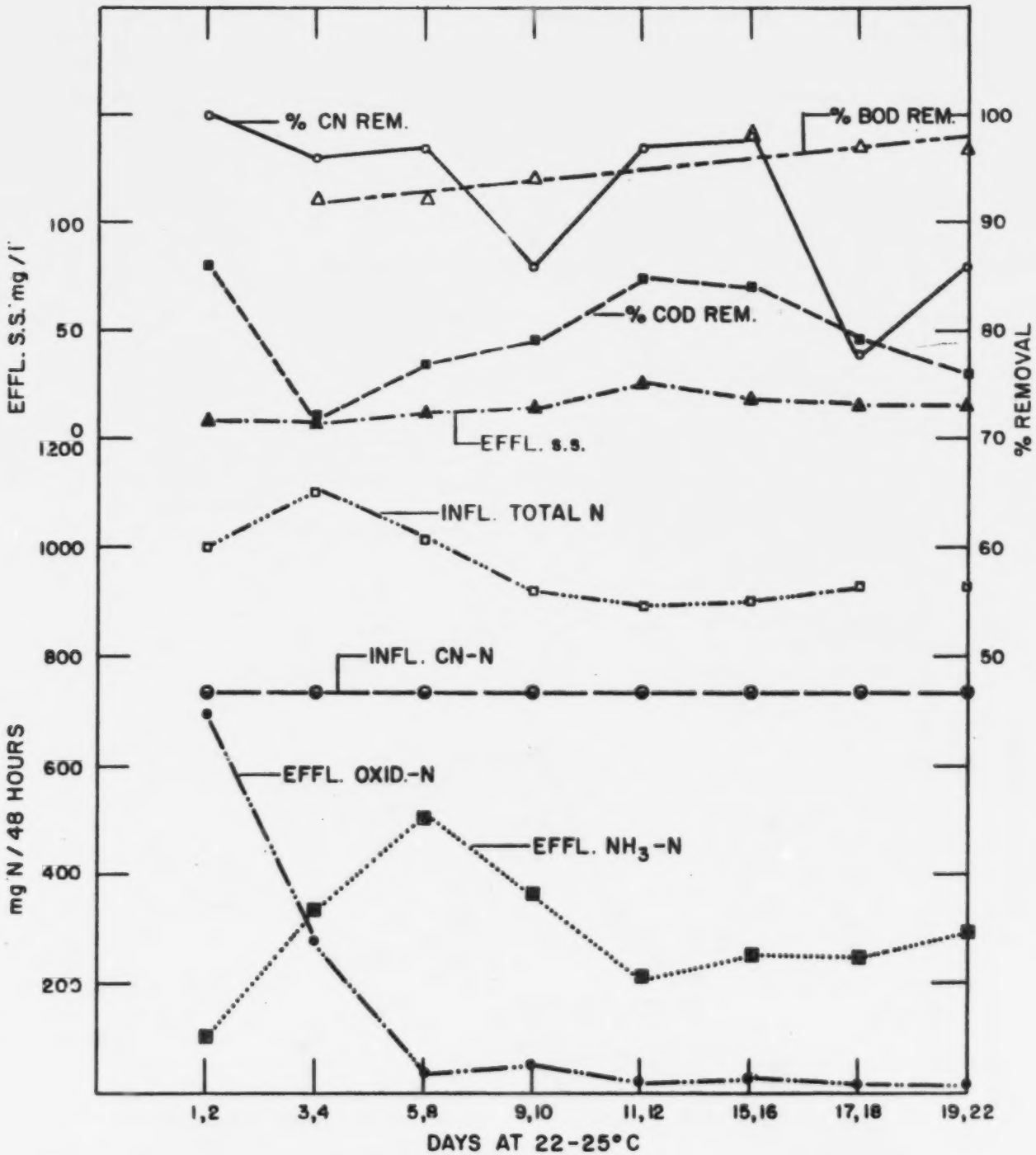
ACTIVATED SLUDGE PERFORMANCE AT 45 mg/l CN

FIGURE 3



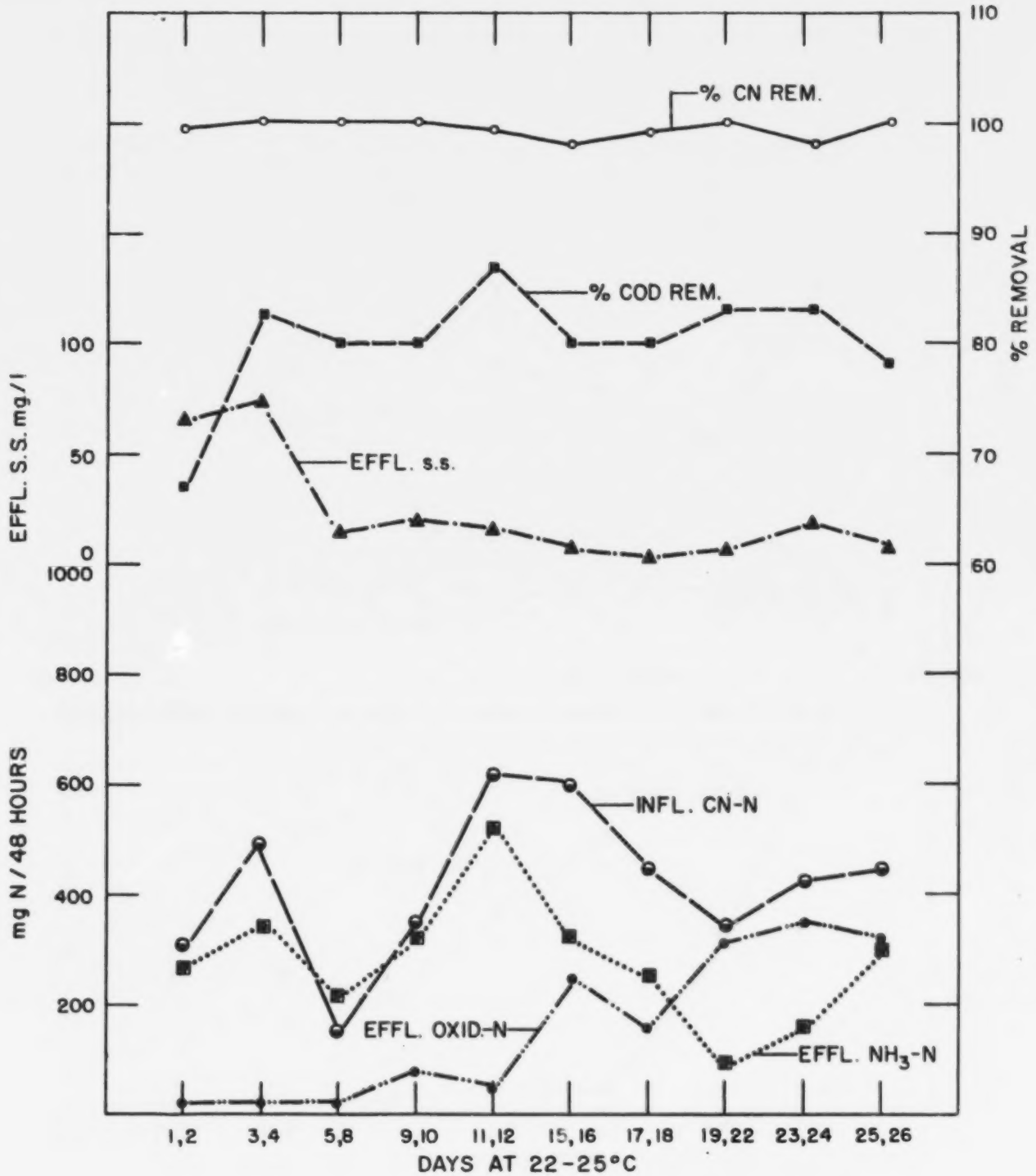
ACTIVATED SLUDGE PERFORMANCE AT 60 mg/l CN

FIGURE 4



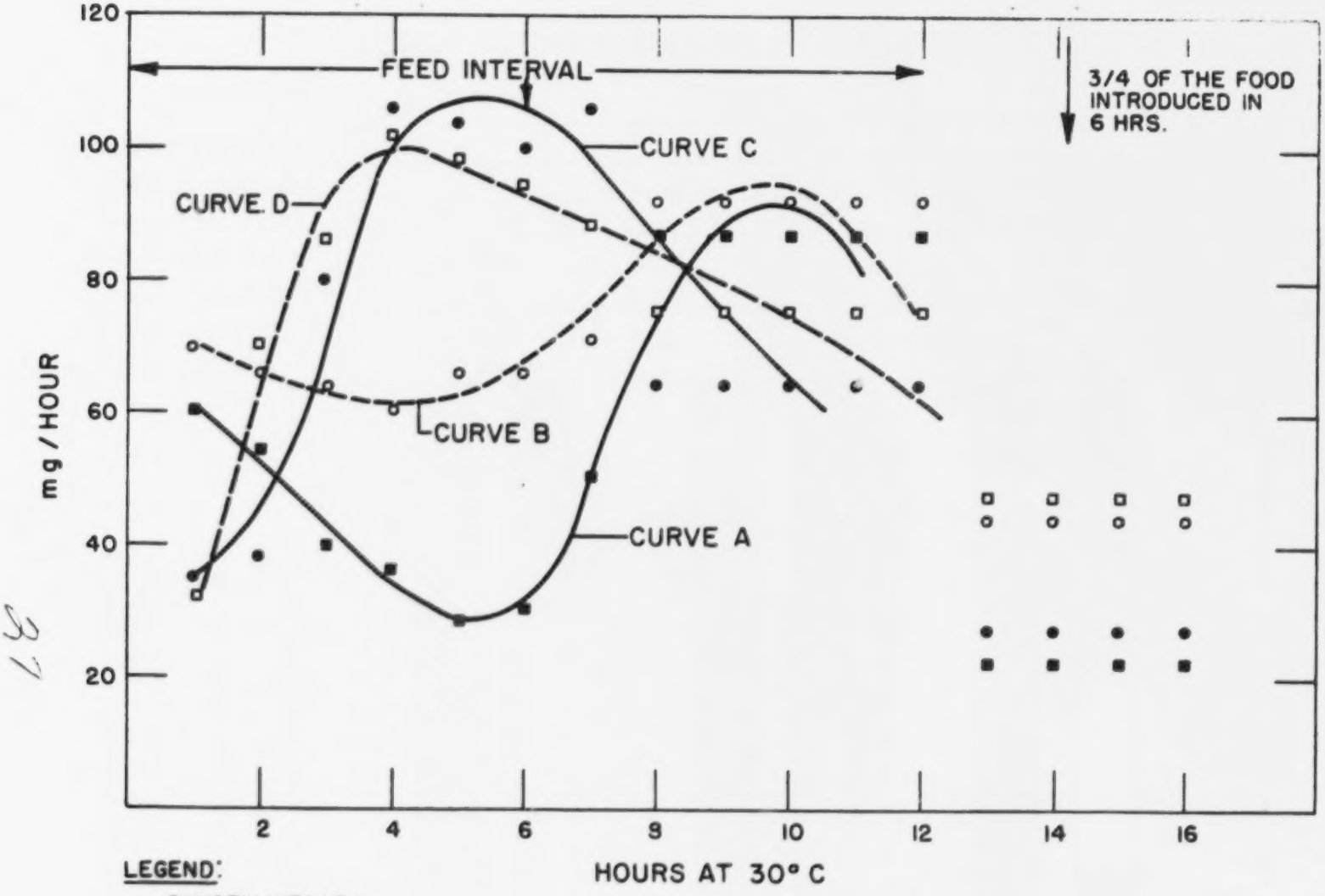
ACTIVATED SLUDGE PERFORMANCE AT 75 mg/l CN

FIGURE 5



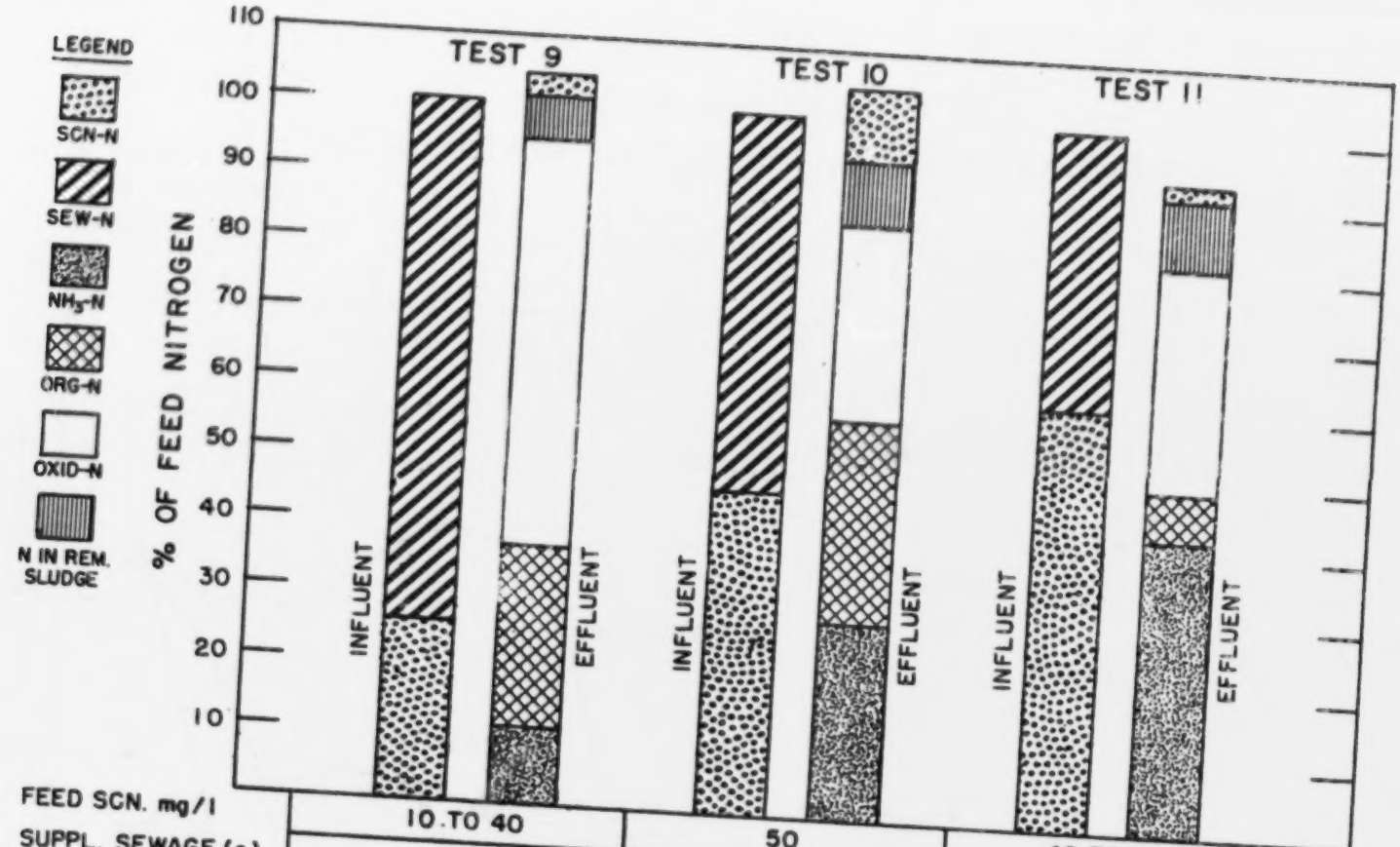
ACTIVATED SLUDGE PERFORMANCE AT 10 TO 75 mg/l CN

FIGURE 6



RESPIRATION TESTS DURING ACCLIMATION
45 mg CN IN SEWAGE / DAY

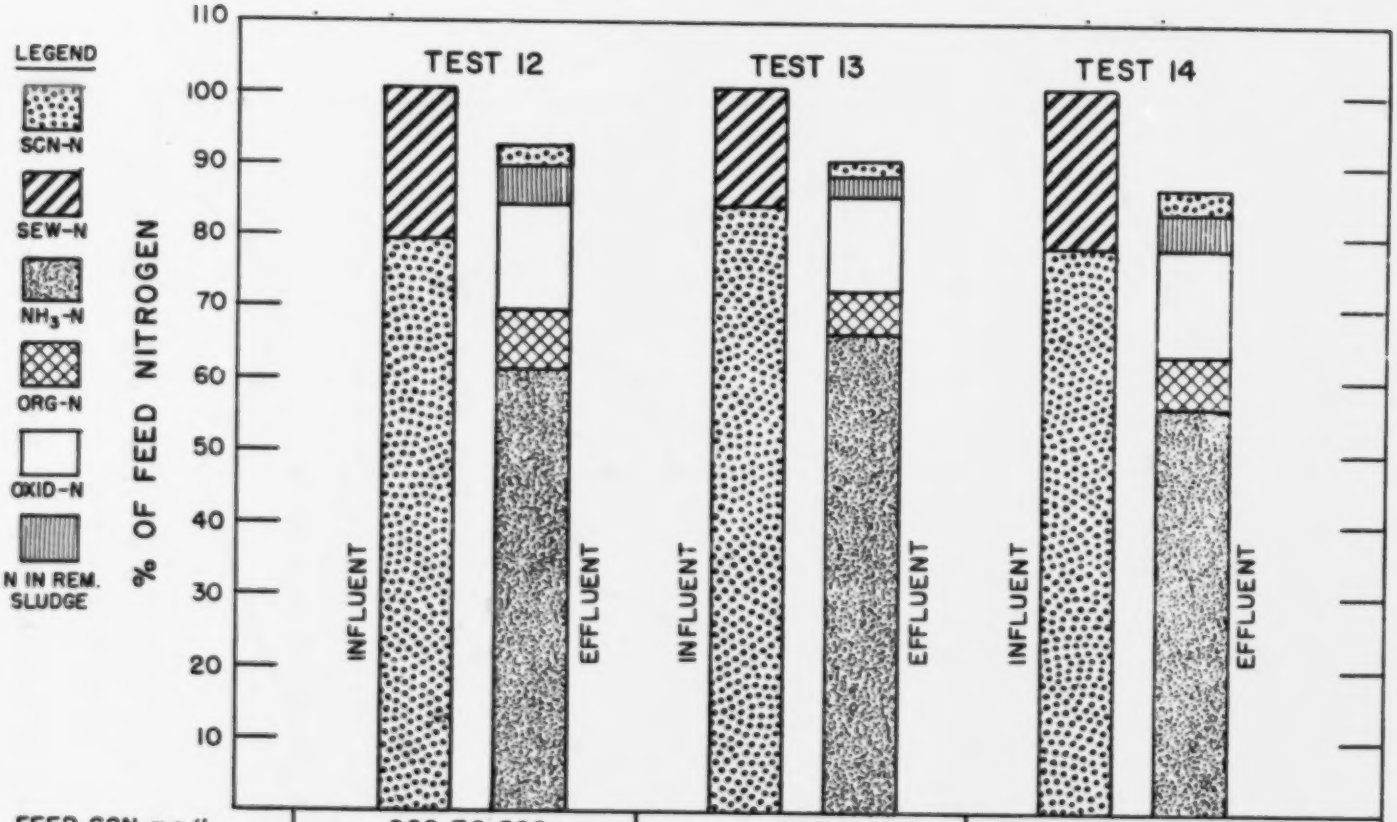
FIGURE 7



	TEST 9	TEST 10	TEST 11
FEED SCN. mg/l	10 TO 40	50	40 TO 160
SUPPL. SEWAGE (s)	YES	YES	YES
SUPPL. DEXTROSE (D)	NO	2g/DAY	1 g/DAY
TOTAL INFL. N. mg	6280	3740	15540
DAILY LOAD RATIO	0.14 TO 0.42/1.0	0.54 TO 0.58/1.0	0.39 TO 0.54/1.0
PRIOR SLUDGE FEED	S	S	S+D+40 SCN
WEEKS OBSERVED	6	3	7

NITROGEN BALANCE ON KSCN ACTIVATED SLUDGE

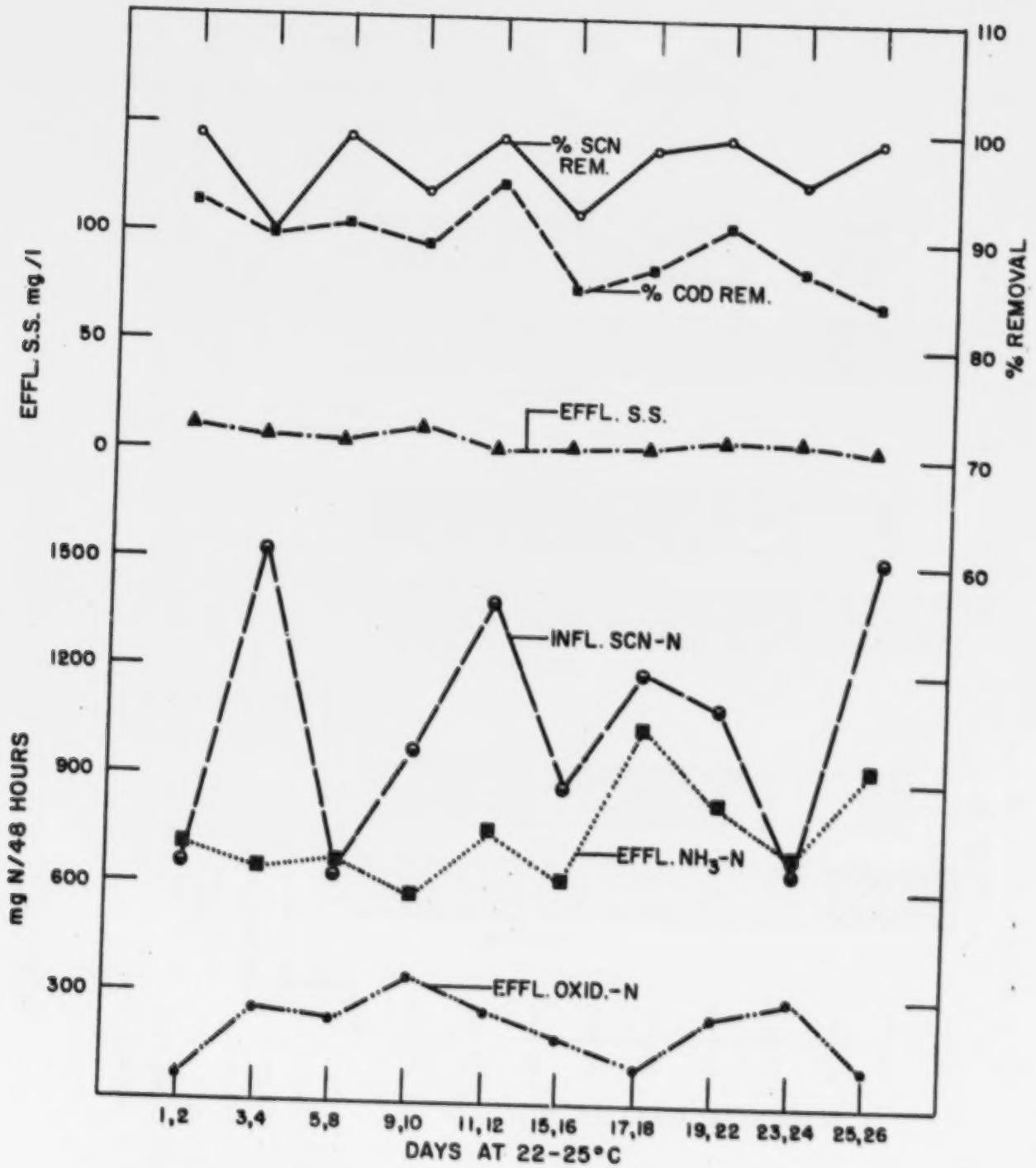
FIGURE 8



FEED SCN mg/l	200 TO 300	300	50 TO 400 VARIED DAILY
SUPPL. SEWAGE (s)	YES	YES	YES
SUPPL. DEXTROSE (D)	1g/DAY	NO	NO
TOTAL INFL. N. mg	20900	18700	13330
DAILY LOAD RATIO	0.46 TO 0.75/1.0	0.53 TO 0.97/1.0	0.47 TO 0.75/1.0
PRIOR SLUDGE FEED	S+D+160 SCN	S+D+300 SCN	S+300 SCN
WEEKS OBSERVED	6	5	4

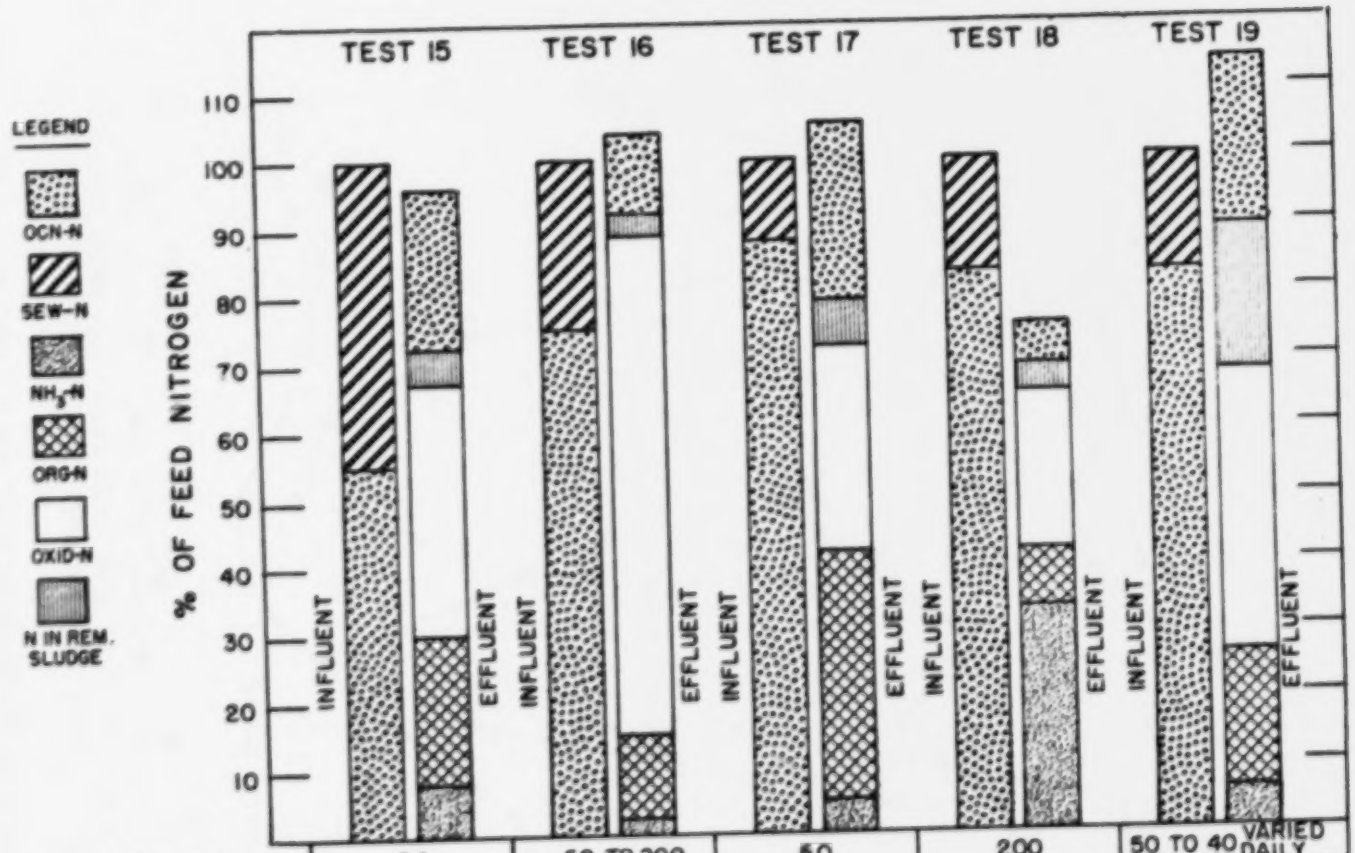
NITROGEN BALANCE ON KSCN ACTIVATED SLUDGE

FIGURE 9



ACTIVATED SLUDGE PERFORMANCE AT 50 TO 400 mg/l SCN

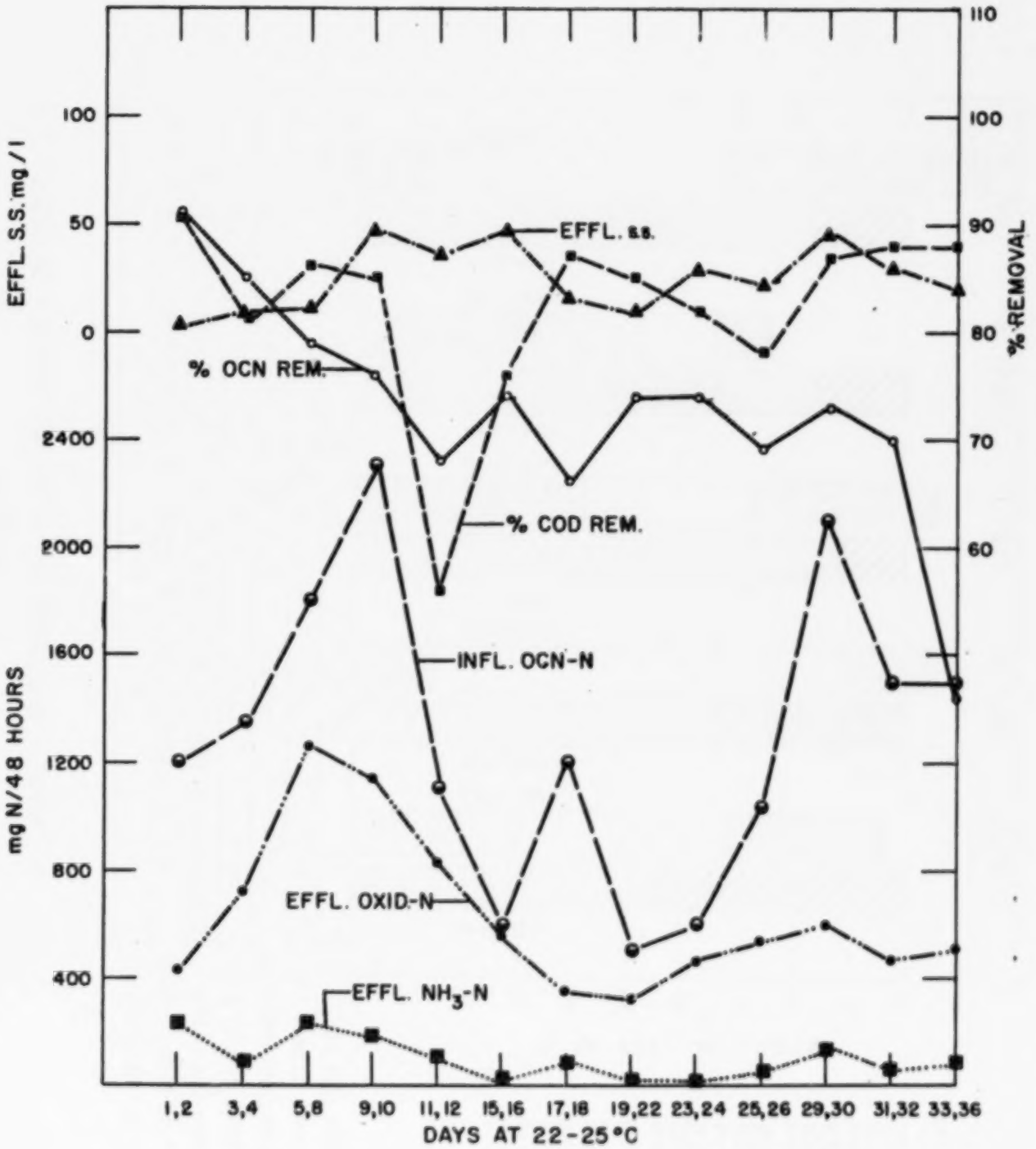
FIGURE 10



	TEST 15	TEST 16	TEST 17	TEST 18	TEST 19
FEED OCN mg/l	50	50 TO 200	50	200	50 TO 40 VARIED DAILY
SUPPL. SEWAGE (s)	YES	YES	1st. & LAST DAY	YES	YES
SUPPL. DEXTROSE (D)	2g/DAY	1g/DAY	2&3g/DAY	1g/DAY	1g/DAY
TOTAL INFL. N. mg	4350	22300	2730	17600	19600
DAILY LOAD RATIO	0.20 TO 0.54/1.0	0.25 TO 0.38/1.0	0.42 TO 0.49/1.0	0.37 TO 0.58/1.0	0.51 TO 0.81/1.0
PRIOR SLUDGE FEED	SEW	S+D+50 OCN	S+D+50 OCN	S+D+100 OCN	S+D+200 OCN
WEEKS OBSERVED	3	8	3	5	5

NITROGEN BALANCE ON KOCN ACTIVATED SLUDGE

FIGURE 11



ACTIVATED SLUDGE PERFORMANCE AT 50 TO 400 mg/l OCN

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FIGURE 12